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ON

PHTHALIC SULPHINIDE

AND

SOME OF ITS DERIVATIVES.

A

DISSERTATION

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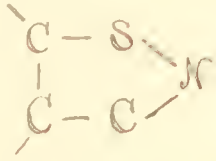
Phthalic Sulphinide.

This substance is one of a group of anhydrides in which the water is regarded as given off between the sulphonamide and a sulphonamide groups in the ortho-position relatively to each other, forming a five-membered ring thus:



Several of these compounds have been well studied, especially benzoic sulphinide, the simplest representative of the series.

Saccharin was discovered by Comstock[1] and more carefully studied by Stokes[2] who obtained several of its salts

1) Ber. chem. Ges. 5, 109

2) do 6, 262

and others and determined the constitution of its acid salts. The present work was undertaken with a view to studying the reactions involved in the preparation of this sulphimide, and some of its decomposition products.

The process employed was that recommended by Stokes, somewhat [illegible] the following stages: from naphthalene the α-naphthalene sulphonic acid was made, and converted successively into the lead [illegible]. [illegible] by [illegible] solution yields the sulphimide. [illegible] obtained had been but a small percentage of the theoretical yield an attempt was made to determine what

condition would yield the most favor-

able result [illegible]

possible.

α-Naphthalene Sulphonic Acid.

The action of concentrated sulphuric acid upon naphthalene yields two sulphonic acids, α- and β, distinguished by their solubility, the solubility of their salts, the characteristic appearance of their lead salts, and by the way in which they burn, the α-acid and salts burning with a smoky flame while the corresponding β-compounds burn like [illegible]

Faraday, Erdmann, Regnault and others.

[illegible]

[1] Merz and Weith, Ber. d. chem. Ges. 13, 476

acids is by Merz who suggests that it might be possible, by preventing the temperature from rising much above the melting point of naphthalene, to secure a product containing but little B-acid; since, when the operation is conducted at a temperature of 160° with excess of sulphuric acid the product contains chiefly B-acid, while at lower temperatures the proportion of A-acid is larger. It is therefore recommended that naphthalene be heated with three parts of sulphuric acid at 80° for 12 hours. Experiments were made with 160 grams of naphthalene and 480 grams of sulphuric acid for 12 hours on a water-bath at a temperature just sufficient to keep the naphthalene melted. The product was converted into the lead salt,

recrystallized and treated with alcohol, in which the α-salt readily dissolves. So large a proportion of the β-salt was obtained that it was thought possible that the α-acid first formed might be changed into the β-acid by the action of the sulphuric acid; since at higher temperatures the α-acid has been found to be completely converted into the β-acid in the presence of sulphuric acid.

Therefore with the same proportions and conditions as before, three experiments were made, heating the mixture one, two and three hours respectively. It was found that by heating two hours the yield of α-acid

---

[1] Merz and Weith, Ber. d. ch. Ges. 3, 186.

from that obtained by four hours heating; but while in the former case [illegible] the end of four hours; but since the action is incomplete, even after further hours heating, and some naphthalene must be recovered in all cases, this is no disadvantage. [illegible] hour gave considerably less x-acid and there was still some of the [illegible]; so that the increase in the amount of B-acid is not sufficient to compensate for the loss of x-acid through stopping the operation [illegible]

the naphthalene in crystalline flakes was mixed in the cold with the acid. On warming it was observed that the [illegible] evidence of reaction below the melting-point of naphthalene. Upon [illegible] it was found that sulphonic acid of [illegible] naphthalene [illegible] to be finely powdered and rubbed into [illegible] and allowed to stand 24 hours, and then brought slowly to a temperature of 80° on the water-bath, and, as soon as it is melted, poured into [illegible] a portable quantity of sulphonic acid is obtained, although less than that of the naphthalene employed. As the result of a number

experiments the following is to be recommended as the best method for the preparation of the acid:

One Kilo of naphthalene, finely powdered, is thoroughly mixed with 750 grams of concentrated sulphuric acid in a mortar and rubbed up occasionally. During the mass is kept at 80° for one hour and then poured 12 liters of water at a temperature of 15°. When cooled to 50° it is filtered through cloth to [illegible] with lead carbonate without warming, since warming gives rise to insoluble basic lead salts which [illegible] the sulphate. After filtering again through cloth, the [illegible]

from the filter and washed by warming for two or three liters of water. The filtrate and washings are evaporated to three liters and filtered hot through a fluted filter. On cooling the crystals which separate out will be found to be almost entirely free from B-salt, and may be used for the preparation of the sulphonamide without further purification.

α Naphthalene Sulphonchloride.

The lead salt above described, after bath was powdered and heated for two hours at 180°-190° to drive off all water of crystallization, and thoroughly mixed with

chloride. The reaction began at once in the cold and was completed by heating on the water-bath until the excess of sodium phosphate and the nuclide were washed by rubbing in a mortar with cold water. If the chloride contains no insoluble matter as is the case when it is made from the sodium salt it [illegible] acted upon in the subsequent treatment with ammonia. The presence of the lead phosphate renders the [illegible] wash, and admits of complete transformation into the amide without especial care. After draining off the washwater the chloride is ready for treatment with ammonia.

α Naphthalene Sulphonamide.

The sulphonchloride prepared as described above was treated with stronger ammonia in a shallow vessel. In a deep vessel it was found that the [illegible] containing an oil difficult to remove. This oil is soluble in water and alcohol [illegible] standing a long time [illegible] standing over sulphuric acid it dries down to a gummy mass. After standing for 24 hours the excess of ammonia was driven off on the water bath and

the amide recrystallized from water. On account of the slight solubility of the amide it was found convenient to crystallize it in portions from the [illegible] and also for various other stages in the preparation of the sulphimide where large vessels were required, I can strongly recommend the use of large [illegible] customary porcelain dishes. They [illegible] light, have convenient handles, [illegible] be rapidly heated and cooled, and [illegible] those which [illegible].

One of these pans was filled with water and brought to active boiling and all the amide put in at [illegible].

filter giving a little time for the water to become saturated, while still continuing to boil through an inverted "funnel" covered with cloth immersed in the boiling liquid. It is desirable to filter the solution as hot as possible since the solubility of the amide appears to increase rapidly near the boiling-point. When cold the supernatant

repeated until all the amide was extracted. One liter of water at boiling more than 5 grams of the amide, nearly all of which separates out on cooling. The mother-liquors do not pay concentration.

The amide thus prepared is white

and has a sharp melting-point, agreeing in properties with the descriptions of Mackopar[1] and Kimberly.[2]

From a Kilogram of naphthalene, about 40 lbs of which was recovered, the yield of recrystallized amide averaged about 375 grams.

Oxidation of the Sulphonamide.

The yield of sulphimide obtained from this oxidation was so small that hopes were entertained that by proper adjustment of proportions and conditions it might be materially increased. A large number of experiments were therefore carried out with a view to determining the effect of varying conditions. After

1) Zeitschr. f. Chem., 1869, 711
2) Ann. Chem. (Liebig) 114, 132.

that the manner of concentrating the

however established.

The first experiments were undertaken with a view to determining the influence

to ten grams of amide being
obtained. The time required for the
reaction at the ordinary temperature varied
from two days to two weeks. In most
of these cases an sulphamide obtained
was the other extreme of temperature. The
potassium hydroxide and permanganate
were dissolved and brought to action
by mixing in a porcelain dish and the

to introduce the [illegible]
hot alkaline solution [illegible]
saturated solution of

finished. The amount of sulphinide obtained was less than in the preceding experiment. Considerable quantities of a ketone acid were formed in this reaction. [illegible] which the sulphinide had been removed) with ether yielded a gummy residue which was soluble in ether and water. With [illegible] which melted at 204°. Upon dissolving this in concentrated sulphuric acid with heat a deep red color appeared, [illegible] presumably the original substance purified, was obtained. This melted at 214°. From these facts there is no doubt that this ketone acid is identical with that described by Henriques (Ber. d. chem. Ges. 21, 1607.)

tives he obtained not pure by conducting the oxidation below 40°. I found this acid [illegible] place for the most part at a temperature lower than 40°. It colors the concentrated filtrate from oxidation red; and when it [illegible] potassium salt of the sulphimide is colored more or less red. By conducting the oxidation as described below none of this ketone acid could be detected. It is worth noting that insufficient quantity of permanganate in hot solution thus appears to give to [illegible] but directed by the lower temperature the ketone acid, an intermediate product between naphthalene and phthalic acid, contains no sulpho group.

It is the common product of the
[illegible] a number of naphthalene
[illegible]; which would seem to
[illegible] the [illegible]
nucleus which is not modified by
substitution in these compounds
[illegible] down under the more violent
action.

At this stage in the oxidation experi-
[illegible]
[illegible] for convenience, one of which was
[illegible]
before while the other by mistake
[illegible] acidification. Both were
hastened in concentration by actual
boiling. On cooling and adding acid
as usual that portion which had been
acidified gave no sulphinide, while

the boiling hydrochloric acid, though
a result quite unexpected, from the
[illegible] split out slowly by the action of
hydrochloric acid.

"To determine the most favorable con-
[illegible] 40 grams of amide was divided
into four equal portions. Two of
these A and B were made up
to eight cc. with water, while to the other two
C and D no water was added. A and
C were then placed in a water bath and B and D boiled
down as rapidly as possible. Each
portion was [illegible]

50 c.c. diluted to exactly 100 c.c., cooled and acidified with 20 c.c. of concentrated hydrochloric acid. After filtering the precipitates were transferred to baker and [illegible] with [illegible] of water. [illegible] salt was as follows:

Acid	A	1.90 grams	
	B	1.75 "	Boiled
Alkali	C	2.10 "	
	D	1.95 "	Boiled

Another similar experiment gave [illegible], showing conclusively that boiling with either dilute acid or alkali [illegible] decomposes the sulphide in some way.

[illegible] concentration was carried on with solutions as nearly neutral as possible and with

quite hot.

An attempt was next made to determine the influence of the concentration of the permanganate solution and the quantity of potassium permanganate, but lack of time and material prevented a complete examination of these points. It seems probable that the amount of potassium permanganate used as indicated below was more than was necessary. The best results however, were obtained in the following:

900 grams of potassium permanganate and 180 grams of potassium hydroxide were brought into an enameled iron pail with 9 liters of water and heated to 55°. 200 grams of dry amide was then stirred in and the source of heat removed. The temperature rose rapidly to 75°. Mechanical stirring, after adding the amide

the temperature down to 60°. The dish was then allowed to stand in a warm place for half an hour, the temperature kept between 60° and 70°, with occasional stirring until the precipitate was completely settled. The supernatant liquor was then decanted off through a filter paper and the precipitate washed by decantation with hot water containing a little ammonium nitrate. After filtering through cloth the manganese hydroxides were returned to the dish and heated nearly to boiling with ten c.c. of water for two hours, with frequent stirring. The precipitate adheres to the dish very obstinately and considerable loss occurs unless this washing be made thoroughly. The filtrate and washwater were concentrated with nitric acid to about 500 cc. and, when cold, acidified with a minimum of nitric acid (sp. gr. 1.42). Into the cold solution the precipitate

was boiled with a small quantity of [illegible], and [illegible] again, since the acid potassium salt is soluble to some extent in water. [illegible] the pure salt thus obtained.

It was noted that the [illegible] was kept within the boiling point without the necessity of cooling. In more concentrated [illegible] the [illegible] the [illegible] the water is much slower and there is no increase in the quantity of sulphonde obtained.

With regard to the formation of phthalic acid it may be noted that the same conditions which gave rise to the formation of the [illegible] acid mentioned [illegible]

to the formation of pikrinic acid. When the oxidation is conducted as last described very little pikrinic acid separates out with the precipitate. The acid however does not always appear as such under these circumstances.

may be reached in the filtrate from oxidation with the addition of the acid potassium salt of the sulphinid. salt of pikrinic acid into an acid potassium salt which is not easily soluble in alcohol but very easily soluble in water. Unless the filtrate from oxidation is very concentrated

hot alcohol, crystallizes from water in groups of thick tapering prisms.

contains neither nitrogen nor sulphur, has
[illegible], and upon heating
with hydrochloric acid and evaporating
[illegible]

By neglecting some of the precautions
mentioned above a somewhat less quantity
of sulphimide may be obtained in consider-
less time. Starting with 350 grams of dry lead
salt I have converted it into the sulphi-
mide, oxidized, evaporated, purified and
recrystallized the acid potassium salt
in two days & eight hours each, obtaining
20 grams of the salt. Double the quantity
[illegible]
in the same time. The chloride was
[illegible]
[illegible] an hour before evaporating off
the ammonia, was precipitated with
water and dried; and at the end of

three hours the unchanged permanganate was reduced by alcohol. Evaporation of the [illegible] the

Conversion of the Acid Potassium Salt into the free Sulphinide.

The salt obtained as above corresponded in appearance and properties with that described by Stokes. Since, according to this investigator, the potassium of this salt reacted upon very [illegible] acid, he recommends the use of the [illegible] to this [illegible] it was thought desirable to ascertain whether conditions could be obtained under which the [illegible] directly upon the acid potassium salt converting it entirely into the sulphinide. A hot concentrated solution of the salt

was poured into a large excess of concentrated hydrochloric acid and heated at a temperature just below its boiling point. On cooling, the precipitate in the form of fine needles of pure sulphide of [illegible] separated out. The filtrate, however, contained a small amount of the sulphide in solution. This was precipitated by passing hydrochloric acid gas through the solution. Too much of the material, and an attempt to recrystallize it from water would result in the formation of [illegible] acid.

By boiling with dilute acid more satisfactory results were obtained. 5 grams of [illegible]

solution; if this be not too concentrated on cooling the the much less soluble [illegible] it may be subsequently observed by the deposit of sulphide. The form in which the acid salt gives rise [illegible] those described by Stokes. If the solution be of such a concentration that crystals begin to appear at about 80°, and the mother-liquor be poured off from the first formed crystals while still hot, these crystals will appear at first sight to be [illegible] but on closer examination more closely resemble triclinic prisms terminated by basal planes. They are made up of thin plates parallel to the basal plane and on account of this structure no satisfactory measurements could be obtained.

Action of Hydrochloric Acid on Phthalic Sulphimide.

Recent experiments in this laboratory have shown that benzoic sulphimide by boiling with dilute hydrochloric acid is converted into sulphamine-benzoic acid and the acid ammonium salt of sulphobenzoic acid. Regarded as successive steps in hydration these transformations may be represented thus:—

$$C_6H_4\begin{cases}SO_2\\CO\end{cases}>NH \qquad C_6H_4\begin{cases}SO_2NH_2\\CO_2H\end{cases} \qquad C_6H_4\begin{cases}SO_3NH_4\\CO_2H\end{cases}$$

By analogy we should expect the same changes to take place in phthalic sulphimide, giving successively

$$C_6H_3\begin{cases}SO_2\\CO\\CO_2H\end{cases}>NH \qquad C_6H_3\begin{cases}SO_2NH_2\\CO_2H\\COH\end{cases} \qquad C_6H_3\begin{cases}SO_3NH_4\\CO_2H\\CO_2H\end{cases}$$

The fact that by boiling in the presence of water phthalic sulphimide is quickly dissolved and that no ammonia is evolved during the process, while ammonium chloride is found in the solution, indicates that the first change does take place, experiments were conducted

acid ammonium salt of sulphophthalic acid.

Five grams of sulphimide were boiled with boiling distilled water for two hours with 250 cc hydrochloric acid, diluted as above. The solution was evaporated to about 50 cc and set aside. The greater part of the sulphimide was thereby recovered. After fifteen the mother liquors stood for 48 hours, and deposited, together with more sulphimide, some well formed crystals which may have been the sulphamine-acid, but they were not obtained in large enough quantity for investigation and analysis. These crystals were prismatic in habit, short and thick, most of them terminated by two broad planes only. The forms observed were only hexagonal, apparently for

a nearly equal development of the ortho-oriented prism and macro-pinacoid.

From subsequent experiments with products similar to those given above it was found that after ten hours boiling the sulphimide is completely changed, and the end product of the reaction [illegible] salt of sulphophthalic acid could not be demonstrated [illegible]. The acid [illegible] crystallized from absolute alcohol in which it is quite easily soluble it returns some of it to impurities and no satisfactory analysis could be obtained. The following facts, however, render it highly probable that the substance at hand was the acid ammonium salt:

1° A solution of the crystallized substance was boiled a short time with an excess of barium carbonate and a barium salt obtained which corresponded to the neutral barium salt of o-sulphophthalic acid as described

by Comstock and again by Stokes. This salt

Calculated for $\left(C_6H_3\begin{Bmatrix}SO_3\\CO_2\\CO_2\end{Bmatrix}_{/2}\right)_2Ba_3$ Found

Ba 45.85 % 45.60 %

2° A solution of the substance in absolute alcohol saturated with dry hydrochloric acid gave no ether of the sulphamine-acid.

3° By warming with caustic alkali ammonia

circumstances, points toward

Action of Potassium Carbonate on Phthalic Sulphinide.

The loss by boiling in evaporating the alkaline solution of the sulphinide indicated a breaking down of the ring under these conditions. To determine this point [illegible] grams of potassium carbonate in 200 cc of water, with reflux condenser. After 10 hours some acid potassium salt [illegible] acidified. Another [illegible] pair after 20 hours boiling no evidence of sulphinide on acidifying. An attempt to determine how far the hydration had gone under these circumstances was defeated by the difficulty of dealing with the products in the presence of so much inorganic matter, since they were [illegible] and insoluble in ether.

conclusively that during the oxidation and subsequent concentration of the sulphimide some loss must be expected if the solutions be allowed to boil.

x Sulphamine Phthalic Acid.

As stated above, this acid was not obtained in the free state in sufficient quantity for identification, if at all. [illegible] it may be possible to obtain conditions of concentration and time of boiling such that a larger proportion of this acid may be obtained. Some of its ethers, however, were obtained.

When benzoic sulphimide[1] in solutions in

[1] Fahlberg and List Ber. [illegible] 50 (6)

alcohol is treated with dry hydrochloric acid

ther of sulphamine benzoic acid

according to the expression

$$C_6H_4\begin{cases}SO_2\\CO\end{cases}>NH + ROH = C_6H_4\begin{cases}SO_2NH_2\\CO_2R\end{cases}$$

of

reaction would be represented:

$$C_6H_3\begin{cases}SO_2\\CO\\CO_2H\end{cases}>NH + 2ROH = C_6H_2\begin{cases}SO_2NH_2\\CO_2R\\CO_2R\end{cases} + H_2O$$

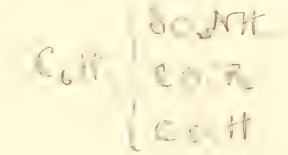
takes place under these conditions, but not the only one. In addition to the well-crystallized sulphamine ether described before there was formed in every reaction in greater or less proportions a substance which

after standing for a month over sulphuric acid, drying down to a clear gum. The conditions under which this appeared in excess were not fully determined; but in

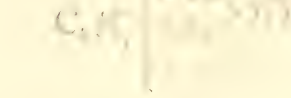
one reaction in which the sulphimide was not thoroughly dried and the treatment with the hydrochloric acid not continued

taking down the sulphimide ring

might look for an intermediate



The alternative would be a saturation of



product of the reaction was either of these substances its barium salt was prepared. Whether made from the product of the reaction in methyl, ethyl or propyl alcohol its appearance

weight, but on heating higher it continued to lose weight with evident signs of decomposition.

constant results upon analysis, varying from 37.12 % to 38.30 % of barium.

Calculated for

	(SO_2H)		(SO_4)
C_6H_4	$(CO_2C_2H_5)$ Ba	C_6H_4 (CO_2) Ba	(C_6H_4) (CO) Ba
Ba	21.26 %	36.07 %	45.55 %

other phenomena observed I think

mixture of the two salts with

are last given.

Alt[d] W[m] Th[s]
sulphamine strychnic acid has been found
to be very easily dissolved even
by action of carbonates, I do not think
that the [illegible]

Di-methyl Ether of x-Sulphamine-Phthalic Acid.

readily in the alcohol, and dry hydrochloric acid passed through it to saturation. Continuing the stream of gas the alcohol was boiled until the sulphamine had nearly all passed into solution. On filtering and evaporation to dryness to expel the hydrochloric acid, a gummy mass remained behind. This dissolved in crystallized in long narrow exceedingly thin plates which showed a tendency upon the filter the mass showed a very characteristic pearly lustre.

more stable than the corresponding ethyl ether. When treated with stronger ammonia and heated on the water-bath it is for the most part unchanged, while the ethyl ether is entirely changed, as described below. After the second recrystallization it showed no further change in the melting point, which was 135°. Analysis for nitrogen gave the following results:

	Calculated for $C_6H_3\{SO_2NH_2, CO_2CH_3, CO_2CH_3$	Found
N	5.14 %	5.06 %

Determinations of sulphur by Pearson's method gave 10.76 %, 10.14 % and 10.48 % while the calculation requires 11.74 % of sulphur. In the last instances the greatest care was taken to secure complete oxidation, but apparently the oxidation was not complete.

It is not probable that the action was methyl alcohol differs from that with ethyl alcohol. The nitrogen analysis

to discredit them. A determination of the

Found

Sulphur 11.74 11.89

Di-ethyl Ether of x-Sulphamine Phthalic Acid.

This was prepared in the same way as the methyl ether above described

It is purified with somewhat greater difficulty than the methyl ether, four or five crystallizations being necessary to bring it to uniform melting point, 101.5° to 102°.

[illegible] standing clears up with the formation of [illegible] bundle arranged parallel to each other.

[illegible] fuses directly on cooling in a characteristic [illegible] the extremity of each becoming [illegible].

By continued treatment with ammonia in the cold the ethyl residues are replaced by amido groups. Whether the ether was saponified by boiling with stronger ammonia was not fully established.

Analysis of this ether gave the following results:

	Calculated for $C_6H_3\{SO_2NH_2, CO_2C_3H_5, CO_2C_3H_5$	Found
N	4.66 %	4.58 %
S	10.64 %	10.15 %, 10.32

Di-propyl Ether of x-Sulphamine-Phthalic Acid.

This ether was made in the same manner as the last described compound. It can be crystallized with great difficulty and then only in part, the remainder settling to the bottom as an oil. Sufficient quantity for analysis was not obtained in crystalline form. Crystals were obtained but

Action of Ammonia on Ethyl-Sulphamine Ether.

The ethyl ether was treated with excess of strongest ammonia in the cold and allowed to stand 24 hours. It was then heated on the water-bath until no odor of ammonia was given off. Upon acidifying it precipitated. It was twice crystallized from water and a pure product obtained.

Carbamine Sulphuride.

The crystals first formed in the hot solution, as described above in the case of the acid-potassium salt of sulphuride, [illegible] axes. The general habit of the crystals when [illegible]

from that of the acid potassium salt and closely resembles that of benzoic sulphinide. [illegible] with an irregular growth line along the [illegible].

[illegible] than the acid potassium salt of the sulphinide. It is slightly soluble in [illegible] ether. It melts at 275° (uncor.). An attempt [illegible] a new compound. It small quantity of the carbamine sulphinide was gently [illegible] in water, and a distinct [illegible] that of the cyanides was given off. The [illegible] fine yellow needles. These were [illegible]

that of fluorescein, which did not dissolve [illegible] adding a little sodium hydroxide to the solution became colorless. It is easily soluble also in alcohol and ether.

[illegible] gave the following results:

Calculated for $C_6H_3\begin{cases}SO_2\\CO\end{cases}>NH$ $\quad CONH_2$ — Found.

N	12.42 %	12.33
		12.15
S	14.17 %	14.38

Analysis also confirmed these results.

From this it would seem that the anhydride ring, [illegible] in the formation of the dye, is opened again in the treatment with ammonia.

From the [illegible]

ethereal salts in general the following reaction:

$$C_2H_3\begin{cases}SO_2NH_2\\CO_2C_2H_5\\CO_2C_2H_5\end{cases} + 2NH_3 = C_2H_3\begin{cases}SO_2NH_2\\CONH_2\\CONH_2\end{cases} + 2C_2H_5OH$$

To determine, if possible what was the action of the ammonia the solution from the treatment of the ether was concentrated to a thin syrup which on cooling was almost filled with crystals. These were analyzed for nitrogen with the following results:

$$C_2H_3\begin{cases}SO_2NH_2\\CONH_2\\CONH_2\end{cases}$$

Calculated for $C_4H_8N_4O_4S$ 17.32 %

Found 17.67 %

losing one molecule of ammonia, taking it up again to form a salt, in which case the stages of the reaction would be represented thus:

$$C_6H_3\begin{cases}SO_2NH_2\\CONH_2\\COOH\end{cases} \qquad C_6H_3\begin{cases}SO_2\\CO\\COOH\end{cases}>NH \qquad C_6H_3\begin{cases}SO_2\\CO\\COOH\end{cases}>N.NH_4$$

or whether the action of the hydrochloric acid was necessary to reform the ring, was not determined. We favoured the latter more probable supposition.

Three salts of the carbamine sulphinide were obtained:

Ammonium salt of Carbamine Sulphinide. —

[illegible] was regarded as this ammonium salt [illegible]

exceedingly soluble in water from which it crystallizes in fine, nearly rectangular needles, apparently orthorhombic prisms terminated by dome faces of one form only.

Barium salt of Carbamine Sulphinide. —

[illegible] upon concentrating a solution of the carbamine sulphinide which had been boiled with barium carbonate. Its solubility [illegible] alike to render its purification by recrystallization practicable with the small amount at hand. It was therefore dried to constant weight at 110° and analyzed for Barium as follows:

Ba 25.00 %

From the following calculated values it-

will be seen that this corresponds more closely to the [illegible] for a salt of the monobasic acid.

Ba calculated for

$C_6H_4\begin{cases} SO_2 \\ CO \\ CONH \end{cases}>N\,Ba_{\frac{1}{2}}$ $C_6H_3\begin{cases} SO_2 \\ CO \\ CO_2 \end{cases}>N>Ba$ $C_6H_3\begin{cases} SO_2NH_2 \\ CO_2 \\ CO_2 \end{cases}Ba$

Ba 13.35 % 37.87 % 36.07 %

Silver salt of Carbamine Sulphimide.

A hot concentrated solution of carbamine sulphimide was treated with an excess of silver nitrate. Almost immediately [illegible] The crystals were not very sharply formed but had a characteristic habit. Those especially which formed upon the side of the beaker were 2 to 3 mm in length and appeared to be orthorhombic prisms [illegible]

in water with great difficulty. 0.26 gr could not be brought completely into solution in half a liter of water by prolonged boiling. The salt was analyzed

31.40

silver salt of carbamine-sulphinide, without water, 32.46 %.

α-Sulpho-phthalic Acid.

Comstock and by Stokes. The free acid,

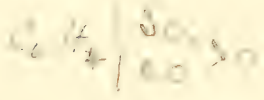
The acid ammonium salt above described obtained by the action of dilute hydrochloric acid upon phthalic sulphinide

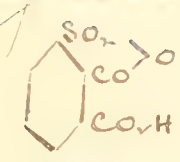
was mixed with an excess of phosphorus pentachloride. In most cases no action was perceptible until the mixture was quite strongly heated. The resulting chloride [illegible] to crystallize this chloride failed. If the washed product, dried over [illegible] in absolute ether remained as an oily mass after the evaporation of the ether. The chloride melts under water below the boiling point, and is slowly decomposed by boiling water. It may be washed [illegible] little loss. By boiling for two hours it is completely converted into the acid, which was identified by making the gelatinous silver salt described by Stokes and also by the barium salt. It is extremely [illegible]

no constant weight was reached.
Then heated several hours longer
at 200°, until the total weight remained constant,
the loss being very slow during the last
hours. The entire loss was 17.5 per cent
acid taken; corresponding nearly
four molecules 22.6 per cent water.
Upon heating to 180° the acid blackened
slightly, nearly throughout. Cupric
chloride to redissolve in water. The
salt passed readily into solution on
boiling, indicating that decomposition had taken
place at a lower temperature.

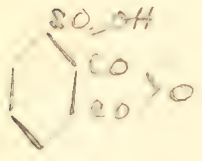
Attempt to prepare an Anhydride of Sulphophthalic Acid.

Recent work in this laboratory has shown





at least might



Some of the sulphophthalic acid, dried for a month over sulphuric acid and having

heated, in vacuo, with sulphuric acid bath, in a small flask provided with a cooling tube. After several hours heating at 175° there was no evidence of sublimation. A sand bath was substituted for the acid bath and the heat gradually increased until the mass within was

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Conclusion.

So much of the time at my disposal was devoted to a study of the reactions involved in the preparation, and the the work afterward taken up was fruitful rather in suggestions of lines of investigation which might be of

tion of the substances; the action
of ammonia, which appears to be different
upon the nitrate and nitrite ethers, and
different when it takes place in hot solution
[illegible]; the course of the reaction in making
these ethers; [illegible]
[illegible] not shown to be in any way related to
the above substances in which they have
[illegible] the formation of fluorescein from the
[illegible]
three lines of investigation which I am
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]

May 6th 1859. My preparation for college
little over a
I completed my preparation
for college with teaching school in
Hennepin County, Minnesota. At the
University of Minnesota I took the
full classical course, receiving the
the following two years I taught
chemistry and physics at Shattuck

My course at this University from
the autumn of 1884 and while

[illegible] Dr. Mendel and Dr. [illegible]
[illegible] Dr. Hawk. [illegible] also
the inorganic chemistry reviews by Dr. Reid